DIELECTRIC MATERIALS FOR ADVANCED ASTRONAUTIC WEAPONS SYSTEMS

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Introduction

We have a better insight today into the technical problems and materials requirements confronting us for advanced aeronautical and space vehicles over what was voiced in 1958 at the Materials Symposium in Dallas. Since that date many long range ballistic missile flights, orbital and space probes, and orbital payload recoveries have been accomplished with varying degrees of success. These pioneering activities have done much to sharpen our understanding of the various materials problems, an understanding of which has helped us to delineate more sophisticated approaches toward accomplishing greater feats.

The purpose of this paper is to outline the environmental conditions under which high temperature dielectric materials might be expected to operate, the potential uses and materials requirements in various engineering devices of Air Force interest, the state of the art in this materials area, and the possible advances that could result from basic and applied research activity.

Further advances in high temperature dielectrics are required in the following important areas:

Re-entry Radomes

Thermionic Energy Converters

Ion Propulsion Engines

Radio and Microwave Frequency Generators

Capacitors for Energy Storage

Insulation for High Temperature Conductors

Corona Suppression

Radar Camouflage

Hopefully, materials requirements for these diverse uses can be met simultaneously by a concerted basic and applied research assault on a few well chosen materials followed by a technological program to produce them in the desired shapes and quantity. In general, the materials available for high temperature mechanical applications are not of sufficient purity, form, or reliability to meet the existing requirements. The basic studies on the nature of brittle fracture, and increasing the thermal shock resistance of ceramic systems should be followed closely.

The High Temperature Environment

The many analytical and experimental studies made for various possible astronautic systems tell us that the re-entry phase is the most demanding upon materials from the heat transfer standpoint while the launch and space phase are most demanding from the reliability and operational performance standpoints.

Figure 1 outlines the heat transfer environment expected for ballistic and manned vehicles re-entering the earth's atmosphere under various trajectories. The ballistic trajectories result in very high heat transfer rates ranging from 1000-5000 BTU/ft^2 - sec, depending upon the magnitude of their ballistic parameter or fineness ration. These heat transfer rates result for only 30 seconds or so and occur at relatively low altitudes. Heat sink and ablation techniques have been used primarily to thermally protect these vehicles from destruction during the re-entry phase. This poses a very serious problem on telemetering antenna and communication devices for this type of weapons system. Manned vehicles, because of "g" limitations, must necessarily re-enter the earth's atmosphere more gradually resulting in re-entry times of about 30 minutes, and in heat transfer rates of 10-100 BTU/ft^2 - sec, considerably reduced, but still very serious when you consider the high temperatures and times involved. Radiation and transpiration cooling appear to be the most desirable methods of thermal protection for these vehicles. Here again antenna housings, radomes, and other dielectric materials next to the boundary layer are exposed to conditions during operation never before investigated.

Figure 2 shows an estimate of the temperature conditions to be experienced by various parts of a manned boost glide re-entry vehicle using the "hot structure" concept. Under the most favorable circumstances present high temperature dielectric materials will be on the fringe of usefulness unless they are located in refrigerated area. It is for this primary reason that we are investigating and improving the temperature limits of high temperature dielectric materials.

Current Technology on Dielectric Materials

Radomes: In supersonic guided missile and space vehicle applications the radome must withstand not only high temperatures, but also severe thermal shock, sudden aerodynamic pressures, vibrational and destructive erosion forces which form its in-flight environment and reach adverse peaks during re-entry. The satisfactory solution of these problems is fundamental to the success of the manned re-entry concept. Table 1 and figures 3 and 4 outline the known properties of several dielectric materials for high temperature antenna housings and radomes. High purity fused silica, alumina, and beryllia appear to have many of the necessary high temperature, thermal shock resistance, and electrical properties necessary for some of the antenna and radome housing applications. The electrical properties of these materials are incomplete and the reliability unknown because it is extremely difficult to make these measurements, especially at microwave frequencies and at elevated temperatures.

A program has been initiated to extend dielectric measuring techniques and apparatus up to temperatures of 3000°F and frequencies up to 50 kmcps to characterize existing dielectric materials. This program will provide long range research into the development of new dielectric materials for use at temperatures of 3000°F and above by attempting to find atoms, molecular groups, and crystal structures which offer materials of special promise for high temperature applications.

Several previous ASD programs which were directed toward the production of high purity dielectric materials should be useful in planning future development work in these areas. In one of these programs, high purity alumina ceramics (having less than 100 ppm impurities) were prepared and some of these were deliberately contaminated by foreign ions. The objective behind the preparation of this series of pure and contaminated ceramic specimens was the isolation of the effects produced by each impurity ion on the dielectric properties of alumina. This information was statistically deduced from measurements of loss tangent and dielectric constant in the frequency range from 10^2 to 10^7 cycles per second and temperatures from 80 to 930°F. A multiple regression analysis of the electrical data provided by these doped specimens has shown that in the order of diminishing influence, the impurities may be grouped as follows: Si, Mg, Ti, Ca, Cr, and Fe (see figure 5). It was also found that high purity alumina has nearly the same positive temperature variation of dielectric constant as far less pure commercial alumina ceramics. Since purification alone was not effective, achieving an invariant dielectric constant was approached by the expedient of introducing into the alumina a second phase having a negative temperature variation of dielectric constant. Since titanites are the most common compounds having the desired negative temperature coefficient; it only remained to choose a representative which would not react with alumina at high temperatures. Fortunately, because the titanite group is more electronegative than the aluminate, such compounds as $CaTiO_3$ and $SrTiO_3$ remain as a stable second phase when fired with the alumina. Preliminary results have shown that a composition containing 10 percent $CaTiO_3$ and 90 percent alumina has an invariant dielectric constant up to about 480°F at 10^7 cps, and losses at 930°F and 10^7 cps somewhat lower than those of Pyroceram 9606.

Another program has been directed toward the preparation of high purity inorganic dielectrics which should possess optimum electrical properties at 1000°F to make them suitable for capacitors and insulators. To obtain optimum properties, inorganic materials for high temperature use must be free of impurities and voids. Elimination of impurities from starting materials as well as the prevention of their introduction during fabrication of the materials into useful forms have been emphasized. Following these principles, good high temperature dielectric properties have been produced in molded or sintered blocks of alumina and boron nitride.

This work on improved high temperature dielectrics for radomes has direct bearing and application to the dielectric materials requirements for thermionic and magnetohydrodynamic energy converters, for ion propulsion devices, and high powered radio and microwave tubes.

Capacitor Materials

The same problems of maintaining purity were encountered, even to a greater degree, in preparing thin films of these materials in a usable and measurable form for capacitors. Thin dielectric films are particularly subject to the effect of imperfections on their properties since the size of such defects, whether they are projections of the metal electrodes or impurity particles, may be of the same order of size as the thickness of the film. For this reason the dielectric properties measured on these films may be grossly affected by these imperfections, in addition to any more generally distributed impurities.

Another characteristic of thin film dielectrics is the greater prominence of interfacial ionic polarization effects, particularly in anodized aluminum. It has not been possible to duplicate the electrical properties of the high purity sintered block material in thin films, however, relatively good dielectric properties have been achieved in these thin films. Another phase of this program was to study thin films prepared by the relatively new technique of arc plasma jet spraying. In this method, a stream of argon gas is passed through an arc where it is ionized and heated. Alumina powder is vibrated into the jet stream where it is heated almost to its melting point and then transported at high velocity to the metal surface where it is embedded. However, a contamination problem from the arc electrodes and nozzle was encountered and the electrical properties of the oxide films were poorer than those of sintered discs made from the same powder.

Corona-Resistant Materials

In addition to the temperature requirement imposed by high speed flight, the behavior of electrical materials exposed to the highly ionizing conditions met in the operation of flight vehicles at very high altitudes must be considered. Commercially available electrical materials tend to outgas under low pressures (200,000 feet altitude or 2mm of Hg absolute), especially under conditions of elevated temperature. As the dissolved gases and volatile components escape, the insulation deteriorates and electrical breakdown and arcing may result. Therefore, electrical equipment which is well designed for ground operation may not operate at all at higher altitudes.

The degree to which electrical insulating materials are attacked by corona seems to depend upon the intensity of the corona discharges, the pulse shape and duration, the time under corona, the surface conduction and charge distribution on the insulation, the environmental gas, its temperature, pressure and flow, and the chemical nature of the insulating material itself. An applied research program is underway to obtain some measurements which reflect the extent of damage which takes place under various corona conditions on a number of insulating materials and to obtain information which will reveal the type of chemical reactions which take place. These results will be analyzed to obtain information about the mechanism of chemical reactions resulting from corona degradation and their relationship to the electrical nature of the discharge and the physical and chemical properties of the insulating materials and their environments.

Insulation for High Temperature Conductors

The ever increasing speeds developed and anticipated by air and space vehicles are creating higher and higher ambient temperatures. Electrical components operating under these higher temperature conditions are seriously handicapped by the lack of suitable insulating materials.

One approach to the problem of high temperature wire insulation is to combine an organic and inorganic coating in the form of a resin containing a powdered glass filler, the resin providing the necessary flexibility. When the insulation system is heated to a high temperature, the resin should burn out and the powdered glass should fuse forming a continuous coating to 1500°F. At 500°F, however, a vitreous enamel coating had poor electrical properties unless a stand-off insulator was provided to keep the viscous molten coating from contact with the bare wire. Aluminum oxide in the form of an anodized coating was selected as the most promising stand-off insulation. This wire was capable of operation at 800°F.

Insulation research at Bell Labs has uncovered a way of forming fluoride coatings on copper, aluminum, and other wire metals that provide excellent insulation at temperatures approaching the melting point of the conductor itself. Even at these temperatures, the insulation is said to retain flexibility and freedom from porosity.

These insulating coatings are formed directly on freshly-cleaned copper or aluminum exposed to the oxidizing carriers of hydrogen fluoride or elemental fluorine at 570 - 1190°F. The thickness of the resulting film depends on the forming temperature, concentration of fluorine, and the exposure time. Aluminum forms a fluoride film that becomes one micron thick in a few moments at 1020°F. The film is reported to adhere to the wire even when bent repeatedly at a 90-degree angle.

According to Bell Labs, the electric insulation values for copper and aluminum films 1-2 microns thick are on the order of 10^{10} and 10^{11} ohms at room temperature. The aluminum fluoride insulation resists breakdown at 450V at 930°F.(The best organic insulation coatings cannot be used continuously above 570°F.)

A porcelain type ceramic coating applied directly to the bare copper wire is another approach. CuO has been incorporated in the base coating and this incorporation has improved the electrical properties. Sheathing these vitreous coatings with organics showed promise as a method for retaining the flexed vitreous coating on the wire.

Radar Camouflage

The Air Force is conducting an active program in radar camouflage, which is concerned partly with the development of radar absorber materials (RAM). Some of the problem areas facing the radar absorber materials designer appear to be solvable only through fundamental materials research.

Generally, radar absorbers depend upon the magnetic and/or dielectric properties of constituent materials to provide electromagnetic impedance matching at the outer surface and dissipation of energy internally. Matching at the outer surface is necessary to insure penetration, and not reflection, of incident energy; since only that energy which penetrates the material may be dissipated.

The required combination of matching and dissipation implies the magnetic and dielectric properties to be complex quantities. These are usually characterized as:

$$\text{permeability}\ (\mu) = \mu' - j\mu'' \ \text{(magnetic properties)}$$

$$\text{permittivity}\ (\epsilon) = \epsilon' - j\epsilon'' \ \text{(dielectric properties)}$$

where μ' and ε' are the real parts and μ'' and ϵ'' the loss factors. The degree of freedom in absorber design is directly dependent upon the ability to exercise independent control of these four parameters.

Absorbers containing magnetic materials ($\mu > 1$ relative to air) have thus far received only moderate attention from engineers intent upon applying RAM to aircraft or missiles because of weight penalties. On the other hand, thicknesses are orders of magnitude below those of absorbers containing no magnetic materials. For this reason, considerable effort should be devoted to development of magnetic absorbers with the hope that weights can be ultimately reduced to useful values. The desirable magnetic properties are usually derived through the use of ferrites (here defined as materials which fall in the broad category of magnetic oxides.)

The state of the art today permits design of high quality RAM with a variety of available ferrites as possible constituents. The big problem, however, is achieving effectiveness over broad ranges of radar frequencies. Limitations on bandwidth are a direct result of the variation of ferrite properties with frequency. The basic factors which determine the ferrite frequency response are not understood precisely, hence there is little knowledge of (a) what determines the μ' and μ'' of a ferrite and (b) what one can do to construct new ferrites with predetermined characteristics. Additionally, RAM containing ferrites are plagued with problems associated with the environment in which it must be used i.e. temperatures which exceed the Curie point, vibrations and strains which reduce the often brittle materials to powder. Only basic research can solve these problems. These ferrite radar absorbing materials could be expected to be useful in the suppression of near field radio and microwave interference also, especially in those installations where several electronic systems are operating in close proximity.

We turn now to radar absorbers which contain no magnetic materials and which are designed on the basis of controlled dielectric properties. That such absorbers exist commercially today is evidence of the variation in constituent materials which is tolerable in the design.

These "controlled dielectric" radar absorbers are inherently thicker than the previously mentioned magnetic types but have several major advantages; they are much lighter weight; have broader bandwidths; and have a flexibility in design which permits choice of constituent materials so that the composite RAM has the desired mechanical and environmental properties.

To design such materials, one needs constituents having a dielectric constant from 1 to 20 and a loss factor from 0 to 20. The maximum values are not exact, but only indicate the range required. To achieve these permittivities today, the normal technique is to impregnate low dielectric constant materials, which act as support matrices, with others of high dielectric constant and high loss. By controlling the concentration of the impregnant, control of the dielectric constant and the loss factor of the finished product is attempted. The addition of certain types of carbon have been found to yield the desired range of values of dielectric properties when combined with a given matrix material. A major reason for an inability to improve the RAM is the inability to control the distribution and concentration of the carbon to the point where predictable and repeatable results can be obtained. Metal particles in place of carbon do not appear to be useful because increasing concentration causes no significant increase in conductivity (which is a measure of the loss factor) until a point is reached where a small increase in concentration causes an extremely rapid rise in conductivity. This occurs when the concentration is great enough to produce electrical contact between particles.

Apparently, a material is needed which is a true semiconductor and which is well-ordered. Carbon is a semiconductor but the best type for RAM use is random in shape and size and therefore it is difficult to control its electrical properties. Research to develop a new semiconducting polymer would appear to be a solution to this problem at least for intermediate temperature applications.

Conclusions

Military requirements are steadily emphasizing operation at higher altitudes and under all weather conditions, as well as requiring these operations to be performed almost completely by automatic equipment. This places stringent requirements on the stability and reliability both in the physical and dielectric properties of materials over a temperature range of -85 to 500°F on current airborne electronic equipment and on re-entry vehicles. This upper temperature limit may extend to 3000°F.

The dielectric materials required for 2500°F antenna housings of Dyna-Soar type re-entry vehicles appear feasible and obtainable with present technology. However, further work in the development of new dielectric materials able to withstand temperatures above 3000°F, as well as characterization and evaluation of these new materials under simulated operational conditions will be necessary to meet the operational requirements for future weapons systems. These high temperature dielectric materials will also be useful as insulators for thermionic and magneto-hydrodynamic converters, for ion propulsion engines, and for high powered radio frequency and microwave generators and amplifiers.

With the growing interest in the sub-millimeter wavelength and infrared region, it is also necessary to consider window materials which will be suitably transparent to these wavelengths yet compatible with the environmental operating conditions of these advanced weapon systems.

With regard to future work on high temperature capacitors, it appears to be necessary to develop new ferroelectric materials and solid solutions which will have higher Curie temperatures than presently available ferroelectric materials, as well as producing high quality thin films of these materials for microminiaturized components.

Further work on high temperature wire insulation is required to develop techniques for applying adherent inorganic dielectric coatings to high temperature conductors and still retain flexibility up to 2000°F.

The development of radar absorber materials is dependent on the complete control of the electromagnetic properties of materials. The theory of design for many types of absorbers is well documented; but until stable materials can be developed and fabricated reproducibly into components having the desired properties, little can be done to improve the current status of radar absorber materials.

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TABLE I

HIGH TEMPERATURE DIELECTRIC MATERIALS

MATERIAL	MELTING POINT (°F)	SPECIFIC GRAVITY	THERMAL EXPANSION (%)	TOTAL EMISSIVITY	THERMAL CONDUCTIVITY BTU/HR/FT/°R	DIELECTRIC CONSTANT (8.4 KMC)	LOSS TANGENT (8.4 KMC)
FUSED SILICA (SiO_2)	3100	1.9	RT 0.10 2000°F 1.35 2500°F 1.40	0.87 0.40	0.9 1.3	3.17 3.28 3.42	0.0002 0.007 0.012
ALUMINUM OXIDE (Al_2O_3)	3700	4.0	RT 0.05 1500°F 0.60 2000°F 0.95 2500°F 1.10	0.78 0.58 0.50 0.44	19.0 4.0 3.2 3.0	8.8 10.1 10.6 11.1	0.0001 0.0004 0.0027 0.0135
BERYLLIUM OXIDE (BeO)	4650	3.0	RT 0.00 1000°F 0.40 2500°F 1.20	0.56	138.0 34.0 10.0	6.24 6.56	0.0004 0.0005
GLASS CERAMIC (PYROCERAM 9606)	2460	2.6	RT 0.00 1000°F 0.25 1500°F 0.36	0.85 0.72 0.67	0.15 1.20 1.30	5.4 5.4 5.4	0.0003 0.002 0.02

RE-ENTRY ENVIRONMENT FOR MISSLE-SPACE VEHICLES

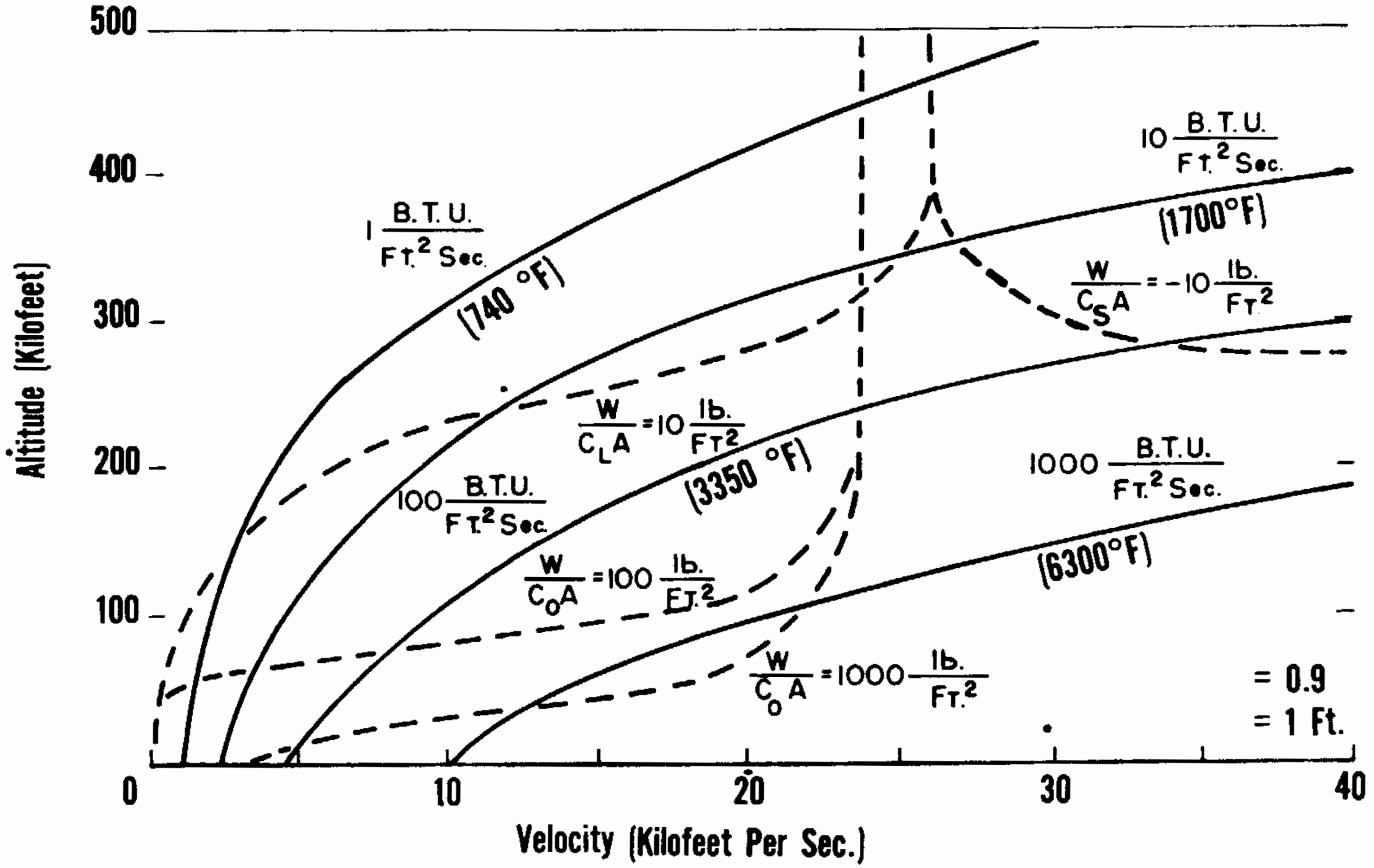

Figure 1.

TEMPERATURE LIMITS FOR HYPERSONIC RE-ENTRY VEHICLES

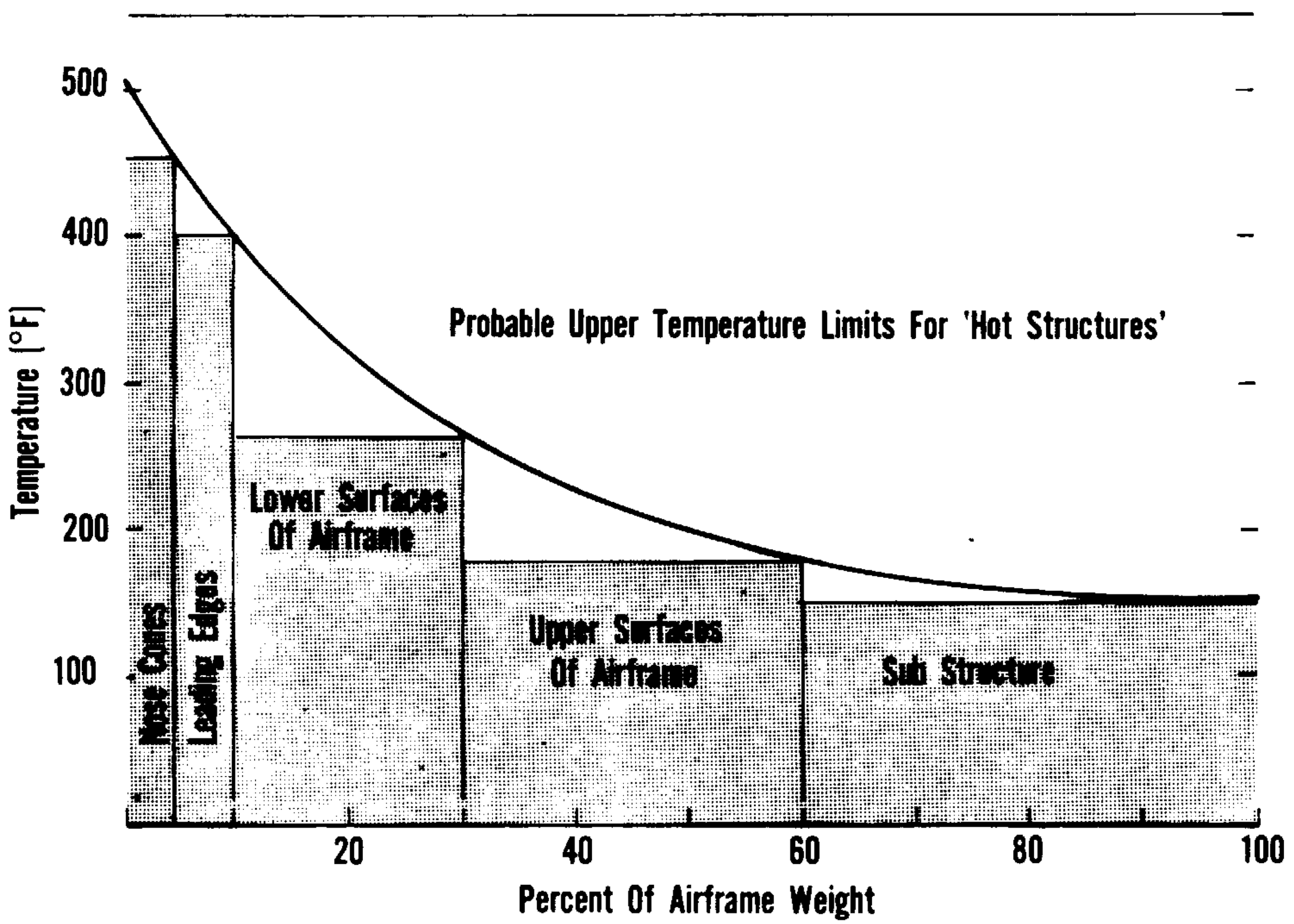

Figure 2.

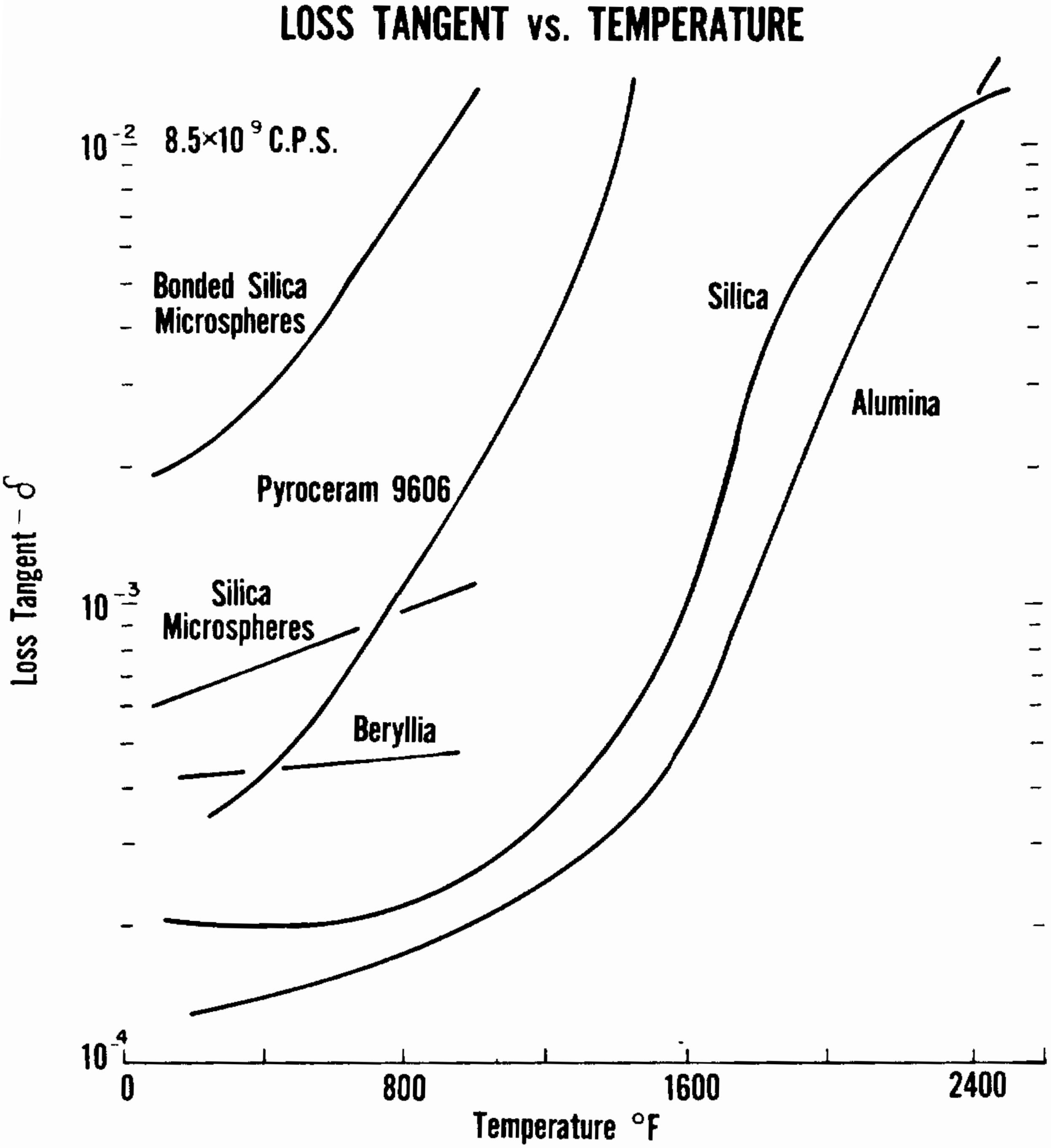
LOSS TANGENT vs. TEMPERATURE
10^{-2}
8.5×10^{9} C.P.S.
Bonded Silica Microspheres
Silica
Alumina
Pyroceram 9606
10^{-3}
Silica Microspheres
Beryllia
10^{-4}
Loss Tangent – δ
0
800
1600
2400
Temperature °F

Figure 3.

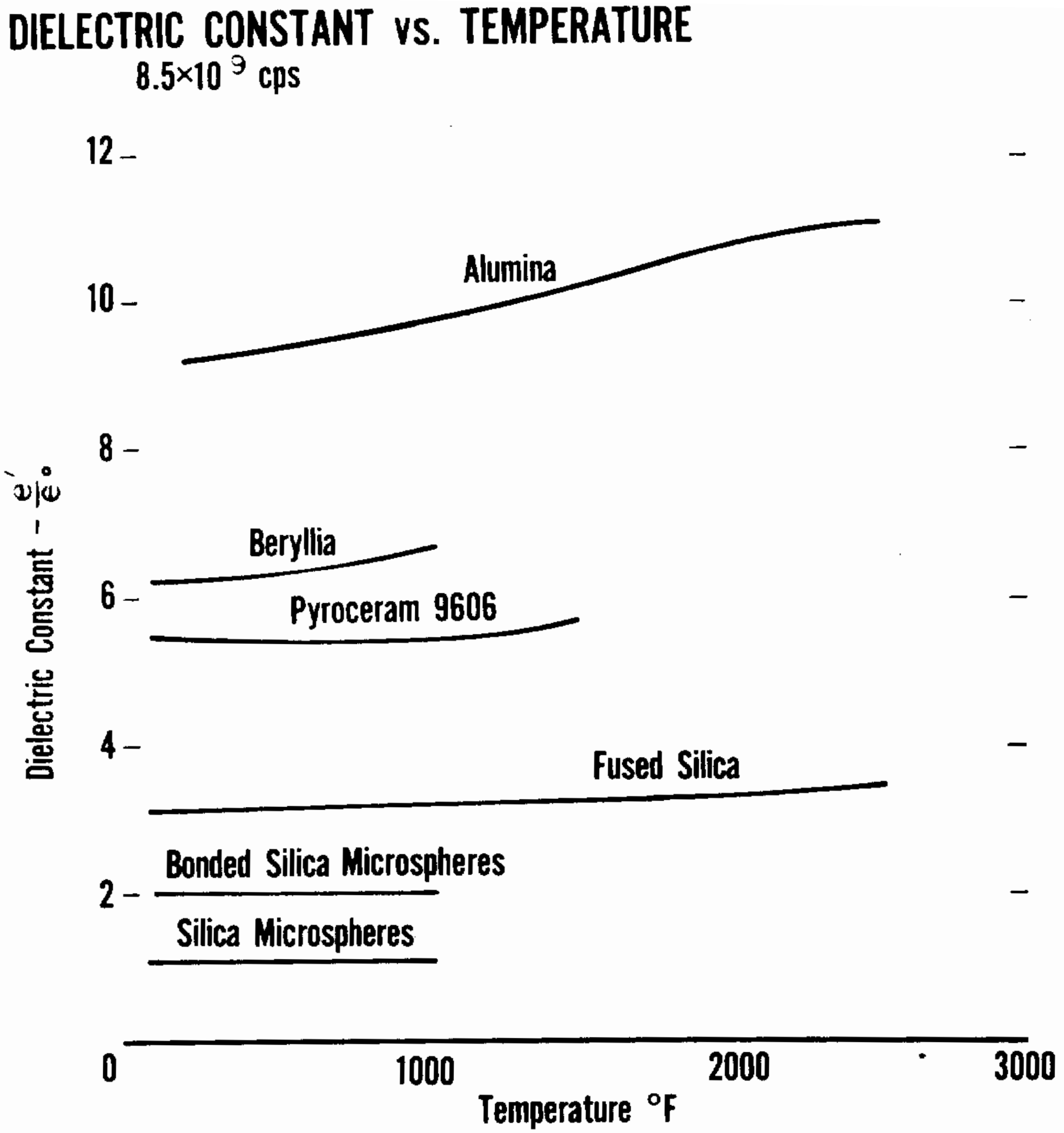
DIELECTRIC CONSTANT vs. TEMPERATURE
8.5×10 9 cps
12
10
8
6
4
2
0
1000
2000
3000
Temperature °F
Dielectric Constant - ε'/ε₀
Alumina
Beryllia
Pyroceram 9606
Fused Silica
Bonded Silica Microspheres
Silica Microspheres

Figure 4.

INFLUENCE OF IMPURITY IONS ON TAN δ (500°C, 10^6 C.P.S.)

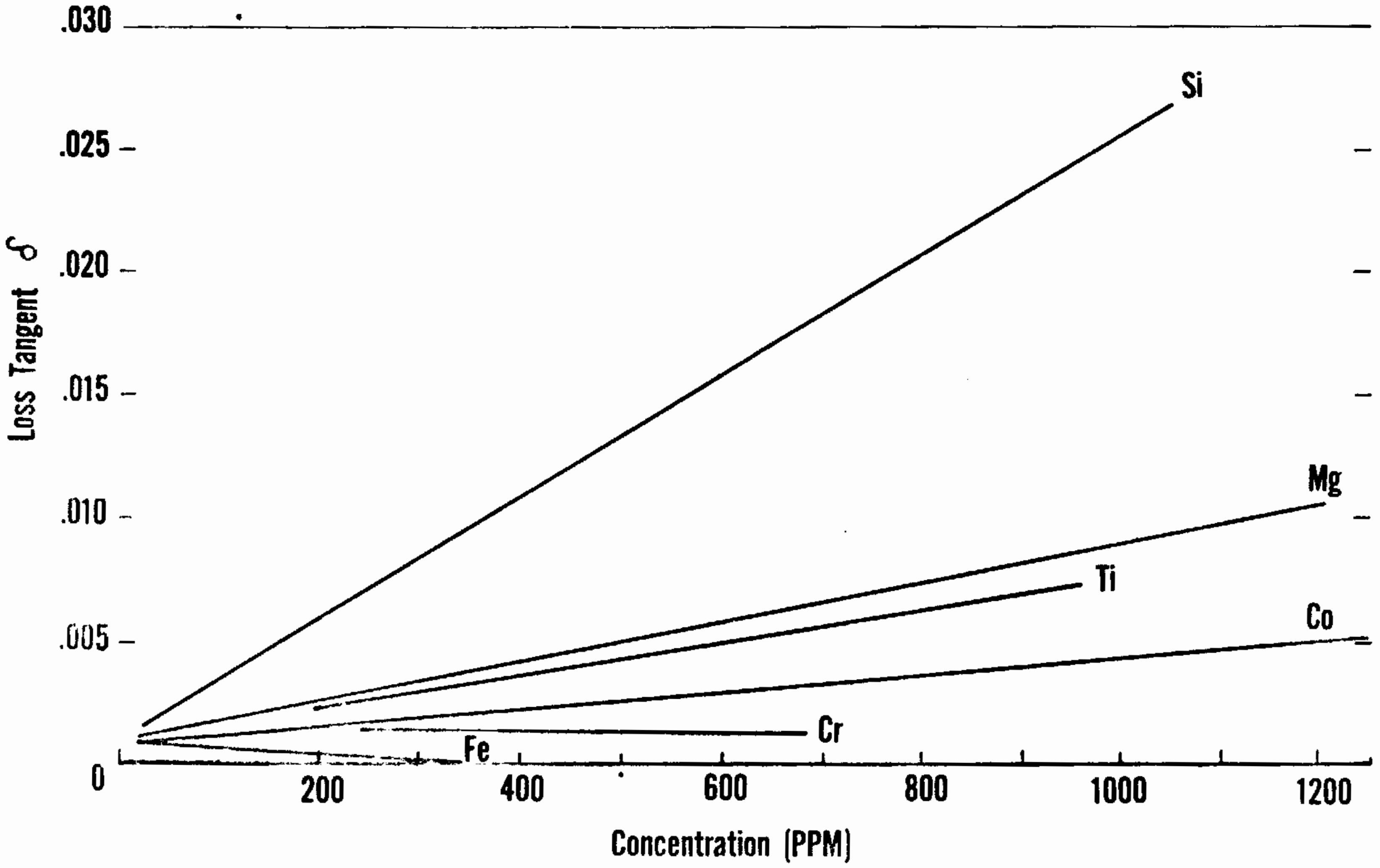

Figure 5.